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Control of Structure and Property in Nanocomposites Comprising Semicrystalline Polymer Matrix and Clay

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Introduction: Nanocomposites based on layered silicates (clays) and polymer matrices have attracted significant attention from the polymer community during the recent years. It has been shown that the introduction of clays can result in drastic changes of morphology, mechanical and rheological properties¹⁻⁶.

In this work structure, property and processing relationships in a series of nanocomposites prepared by *in-situ* polymerization of nylon-6 in montmorillonite clay and by melt-blending of polyethylene-vinylacetate (EVA) copolymers with cloisite[®] organoclays have been investigated by using the combined techniques of simultaneous synchrotron small-angle x-ray scattering (SAXS), and wide-angle X-ray diffraction (WAXD), rheology, DSC and thermal mechanical analysis. The purpose of this work is to gain fundamental insights into the control of structure and processability in nanocomposites, prepared by different pathways, where the clay particles are largely exfoliated. It was shown that the structure of the crystalline domain in EVA copolymers was not significantly affected by the presence of organoclay. In contrast, the introduction of organoclays drastically altered the structure of the crystalline phase in nylon-based systems. We propose that the observed difference may be related to the high content of polar groups in the crystalline domain of nylon-6, while the crystalline phase in EVA is formed by non-polar methylene segments. The structure study of nylon-based nanocomposites have been published by us recently⁷⁻⁸. In EVA-clay nanocomposites, we found that exfoliated clay particles formed a 3-D network structure in the molten state, which significantly affected the rheological behavior. This behavior can be attributed to the reduction of local viscosity at high temperature, which facilitates rotational diffusion of clay particles allowing a "jamming" phenomenon and thus resulting in pseudo-solid rheological properties.

Methods and Materials: EVA nanocomposites were prepared by melt-blending of EVA co-polymers with organoclay using Brabender melt mixer at 160°C. Two types of organoclays (C6A and C20A) were used in preparation of EVA nanocomposites, which were obtained from Southern Clay, Inc. All clays contained the same mineral base (montmorillonite clay cloisite). The content of surfactant in organoclay (N,N di-methyl di-hydro-tallo ammonia chloride) varied from 45 wt % (in C6A) to 30 wt% (in C20A). EVA samples were received from Du Pont: EVA8 contained 8.3 mol% of vinylacetate (VA) co-monomer, EVA3 contained 3.1 mol% of VA content. Weight-average molecular weight (M_w) for EVA8 was 110,000 g/mol, for EVA3 was 150,000 g/mol.

Montmorillonite/nylon 6 *in-situ* polymerized nanocomposite materials and pure nylon 6 polymer (Nyl6) were obtained from Ube Industries, Ltd (Japan). The clay content in samples under this investigation was 2 wt% (labeled NCH2) and 5 wt% (NCH5). The weight average molecular weights of the nylon-6 polymer in nylon nanocomposites were 22,200 (NCH2) and 19,700 (NCH5) g/mol, respectively. All materials were used as received from the manufacturer.

TGA measurements were performed using TGA 2950 (TA Instruments). Measurements of the complex dielectric permittivity, $\epsilon^* = \epsilon' - i\epsilon''$ were performed over a frequency (F) window of $10^{-1}\text{Hz} < F < 10^6\text{Hz}$ in

Results: Pronounced effect of organoclay on the structure of the crystalline phase was detected in nylon nanocomposites. For example, nylon-6 exhibits predominantly α -phase from room temperature to melting with a gradual shift in chain-chain and sheet-sheet spacings from $\sim 100^\circ\text{C}$ to melting. The presence of layered silicate stabilizes the dominant γ -crystal phase, which persists until melting. The temperature dependence of the total crystallinity and the relative fractions of α - and γ -phases were also shown to be strongly dependent on the layered silicate content and the interaction between the nylon 6 and the silicate layers. In contrast, both melting and crystallization behavior were not significantly affected by the presence of organoclays in EVA. Dielectric investigation showed no significant change of glass transition temperature and local segmental mobility of EVA below melting temperature (T_m). However while the rheological behavior of EVA above T_m was typical of polymer melts, EVA-organoclay nanocomposites exhibited pseudo-solid like rheology in small-strain oscillatory shear experiments, yet they were able to flow under a steady shear. This pseudo-solid behavior became more pronounced at higher temperatures.

Conclusions: We propose that in the solid EVA nanocomposites, clay particles are predominantly confined to the amorphous phase, whereas in the molten state, exfoliated clay particles form a 3-D network structure. We suggest that the reduction of local viscosity with the temperature increase facilitates rotational diffusion of clay particles allowing a "jamming" phenomenon leading to pseudo-solid rheological properties.

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